Stanford University

# Insights from Mesoscale Characterization Guide Rational LIB Design

Principal Investigators: Yi Cui, William Chueh, Mike Toney
SLAC National Accelerator Laboratory

Annual Merit Review
DOE Vehicle Technologies Program
Washington, DC
5-9 June, 2017

ES334

# Overview

## Timeline

- Start Date: Q2 FY16
- End Date: Q2 FY18
- Percent complete: 45%

## Barriers

- Barriers addressed
  - Advanced *in-situ* diagnostic to pinpoint and predict failures in batteries
  - Screen new battery chemistries using advanced diagnostic
  - Electrode lifetime

## Budget

- Total project funding: 100% DOE
- FY16 Funding: $ 300K

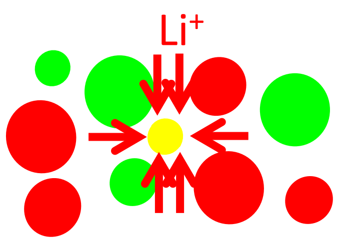
## Partners

- PIs: Yi Cui, Will Chueh, Mike Toney
- Collaborators:
  - Wanli Yang (LBNL ALS)
  - David Prendergast (LBNL TMF)
  - Industry (materials)

# Objectives & Relevance

**Objectives**: Develop and utilize a correlative microscopy platform to investigate the (de)lithiation dynamics of LMR-NMC and NMC, with the specific goal of understanding factors that determine the rate capability and degradation mechanisms at the secondary particle, single primary particle, and atomistic length scale.

*Macroscale*: Hot Spots



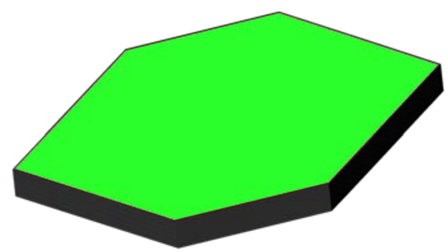

High current density

*Lithium-rich* *Lithium-poor*

*Actively Intercalating*

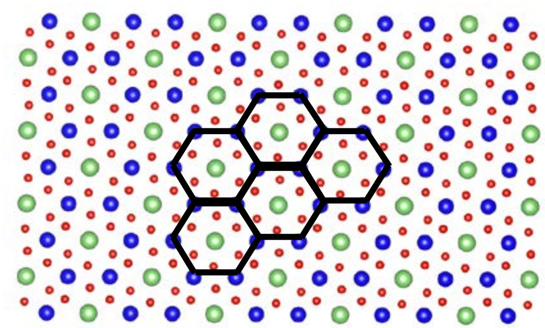
→ **degradation**

*Mesoscale*: Kinetics & Chemo-mechanics



→ **rate capability & lifetime**

*Atomic*: Redox



Ni(IV) $O^{2-}$

Ni(III) $O_2^{2-}$

→ **voltage, hysteresis & capacity**

# Objectives & Relevance

**Relevance**:

- Understand atomistic and mesoscale factors that lead to capacity & voltage fading in layered oxide cathode (LMR-NMC & NMC)
- Develop diagnostic tools that reach new length scales not previously available

**Impact**:

- Enable accelerated materials development time by understanding capacity & voltage fade mechanisms
- Provide new information to design fast charging protocols and to improve power density

# Milestones

**FY16:**

- Development of correlative microscopy platform for imaging LMR-NMC cathodes. **Achieved**.

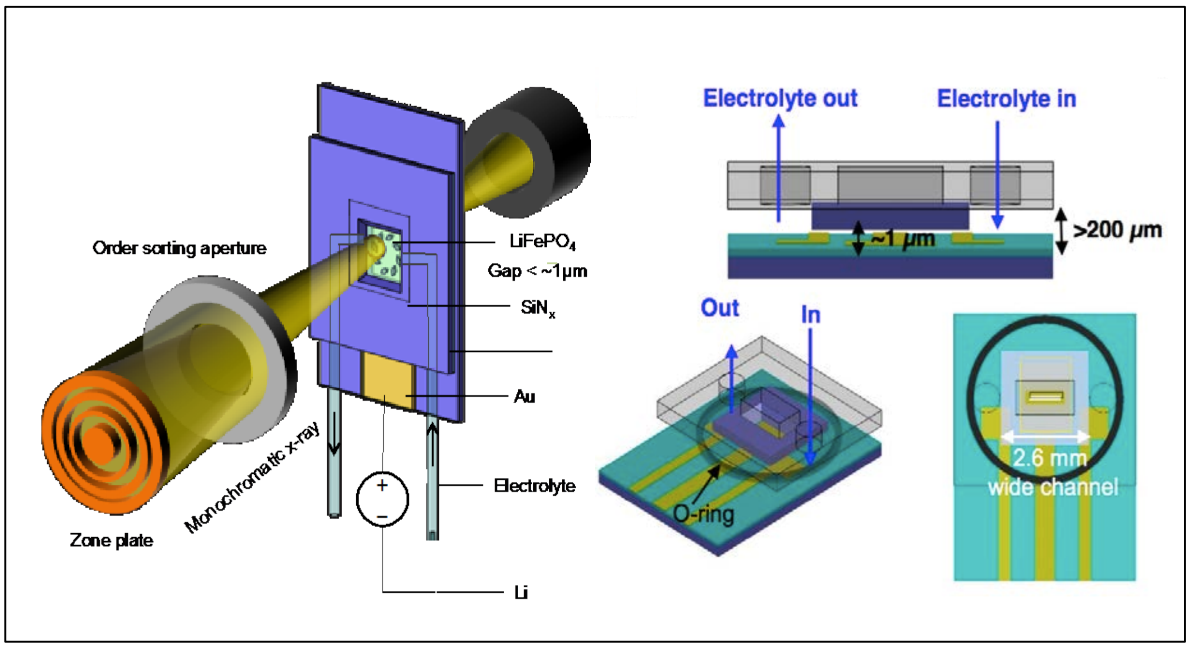
**FY17-18:**

- Synthesis and characterization of well-faceted NMC and NMC particles. Demonstrate *in-situ* single particle imaging with spectro-ptychography of NMC. **Ongoing.**
- Use of correlative microscopy platform for imaging LMR-NMC and NMC cathode hotspots. **Ongoing.**
- Spectro-imaging of single NMC particles. **Ongoing.**
- *Ex-situ* variable temperature (-20 C to +80 C) spectro-imaging of LMR-NMC particles. **Ongoing**

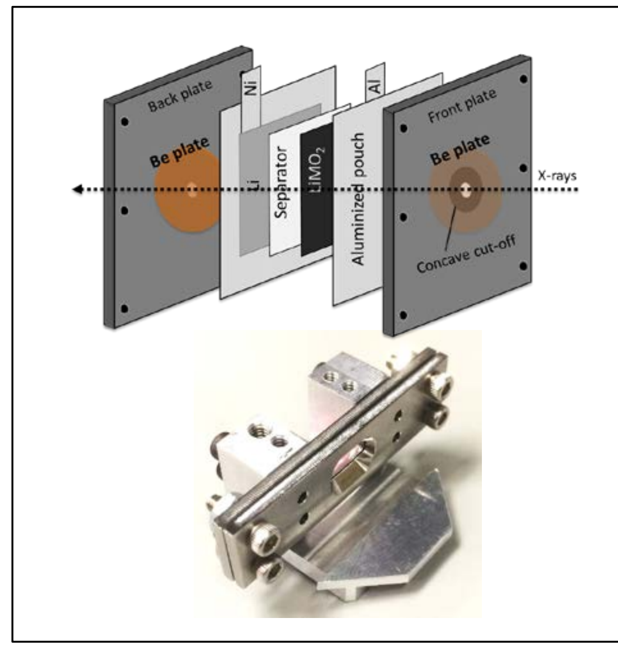
# Approach

- Develop & utilize in-situ & ex-situ X-ray spectro-microscopy to relate local chemistry and microstructure evolution to battery electrochemical characteristics (voltage, capacity/voltage fade, and activation)
- Correlate with other characterizations such as diffraction & electron microscopy.

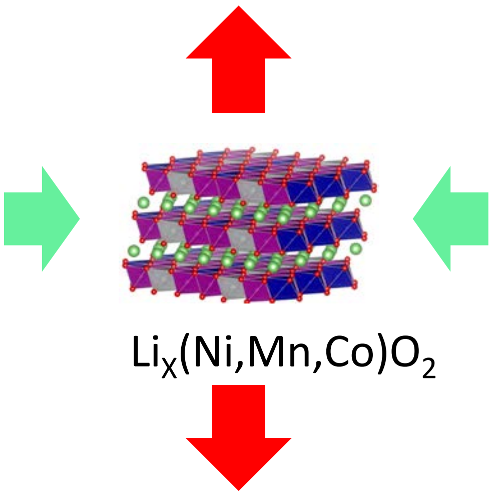
Soft X-ray Transmission (< 500 nm penetration)



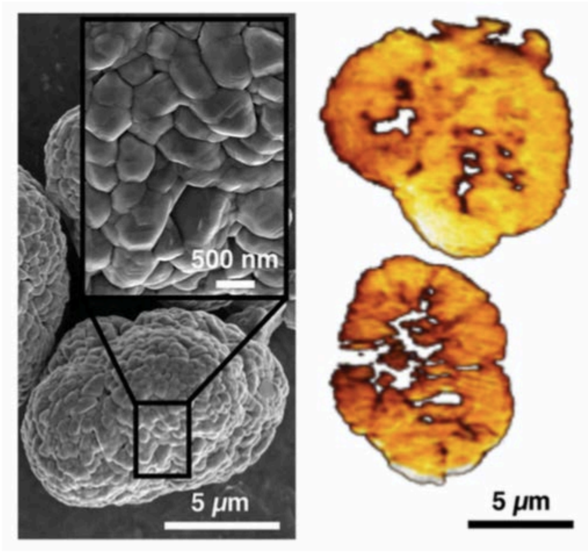

Hard X-ray Transmission
(< 50 µm penetration)

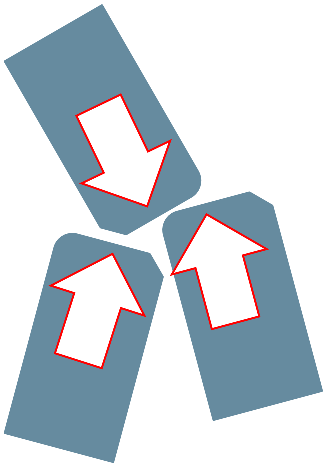


# Technical Progress: Anisotropic chemical expansion
## *Local overcharging at C/110 in NMC111*



$Li_X(Ni,Mn,Co)O_2$



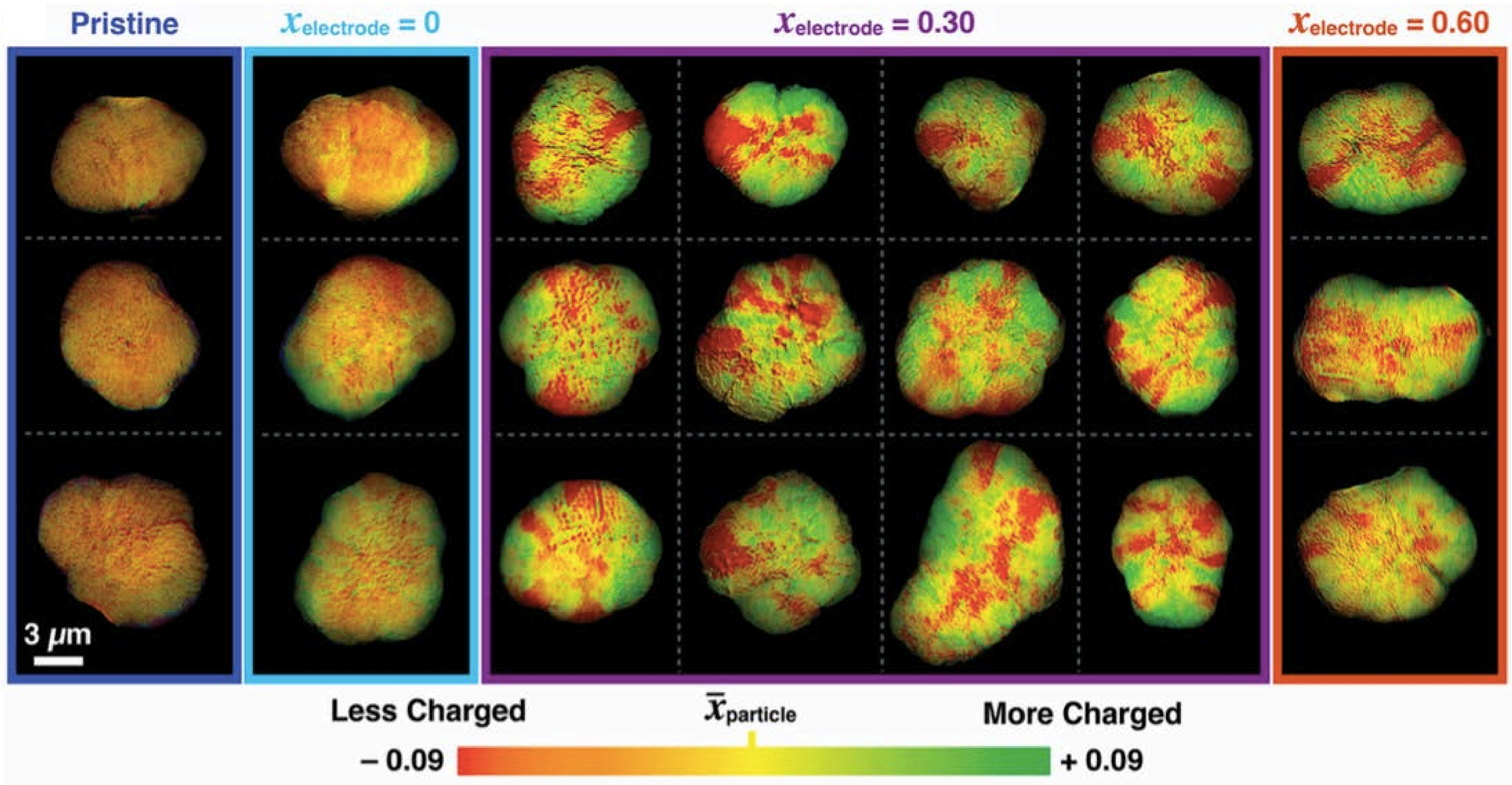
Single primary particle

Secondary particle

- All layered oxides and graphite exhibit anisotropic chemical expansion, meaning that lattice expansion/contraction upon charging/discharging is not the same along different crystallographic directions.
- Preferred orientation in the secondary particle during co-precipitation synthesis of layered oxides give rise stress concentration points throughout the secondary particles, resulting in non-uniform strain.

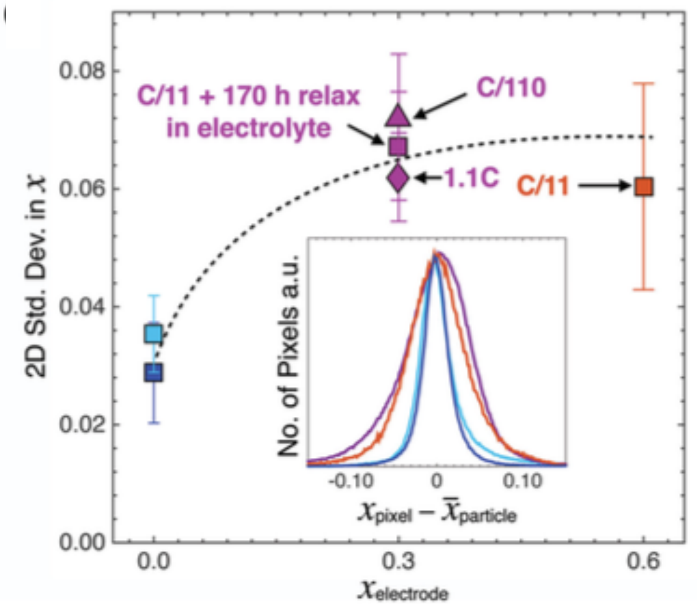
# Anisotropic chemical expansion in NMC111: *Local overcharging at C/110*

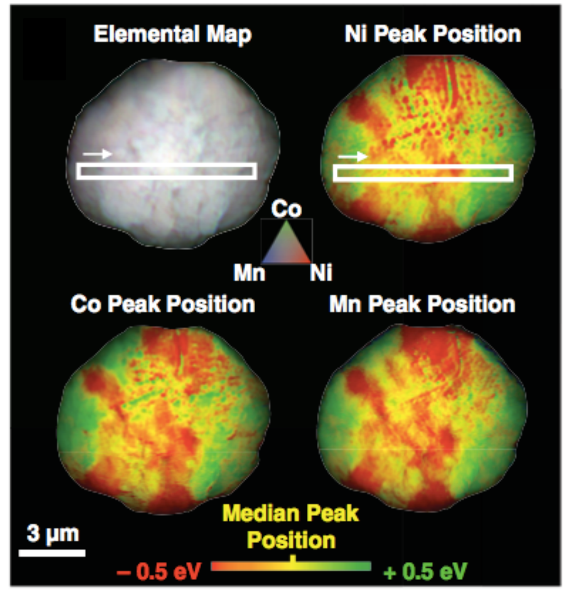
$Li_{1-x}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$ Secondary Particles at C/110

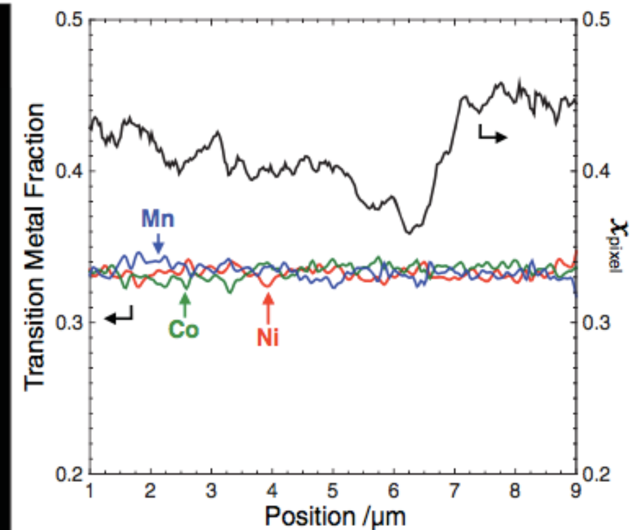



- X-ray microscopy revealed significant SOC heterogeneity at 50% and 100% SOC within secondary particles even when cycled at C/110.
- > 10% <u>local</u> overcharging beyond electrode average SOC.

# Anisotropic chemical expansion in NMC111: *Local overcharging at C/110*



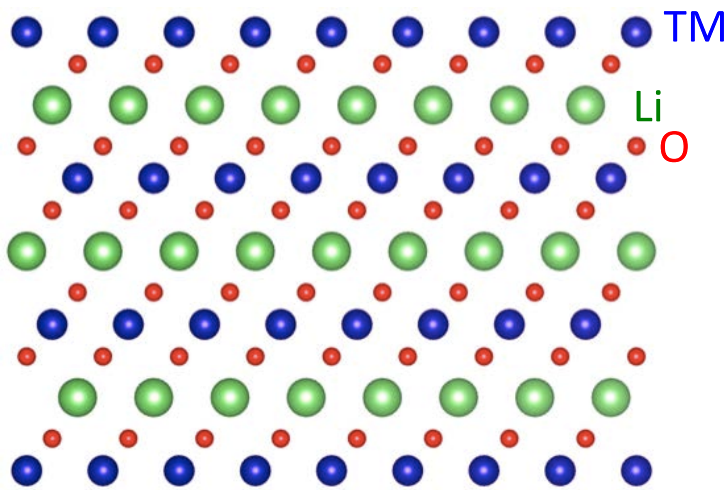




- No detectable composition variation & no kinetic limitation.
- Variation in SOC in ~ 1 micron domains (hot spots) exceeds 10% and is connected to volume-change-induced stress and the associated shift in the local open-circuit potential.

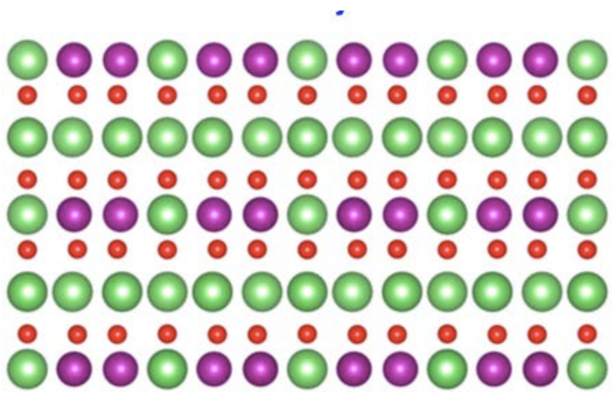
**Take Home**: The induced stresses and accompanying SOC heterogeneity have detrimental effect on the material cycle life by accelerating secondary particle fracture and resulting in locally overcharged domains at the cutoff voltage.

# Lithium-excess layered oxides: *approaching 1 Li/formula*

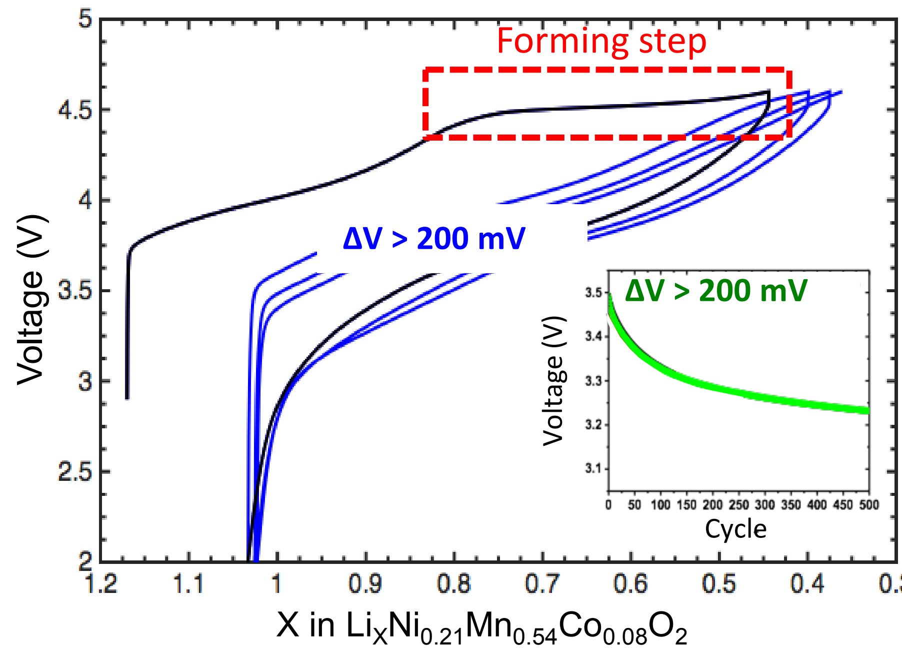
Li stoichiometric




Li excess



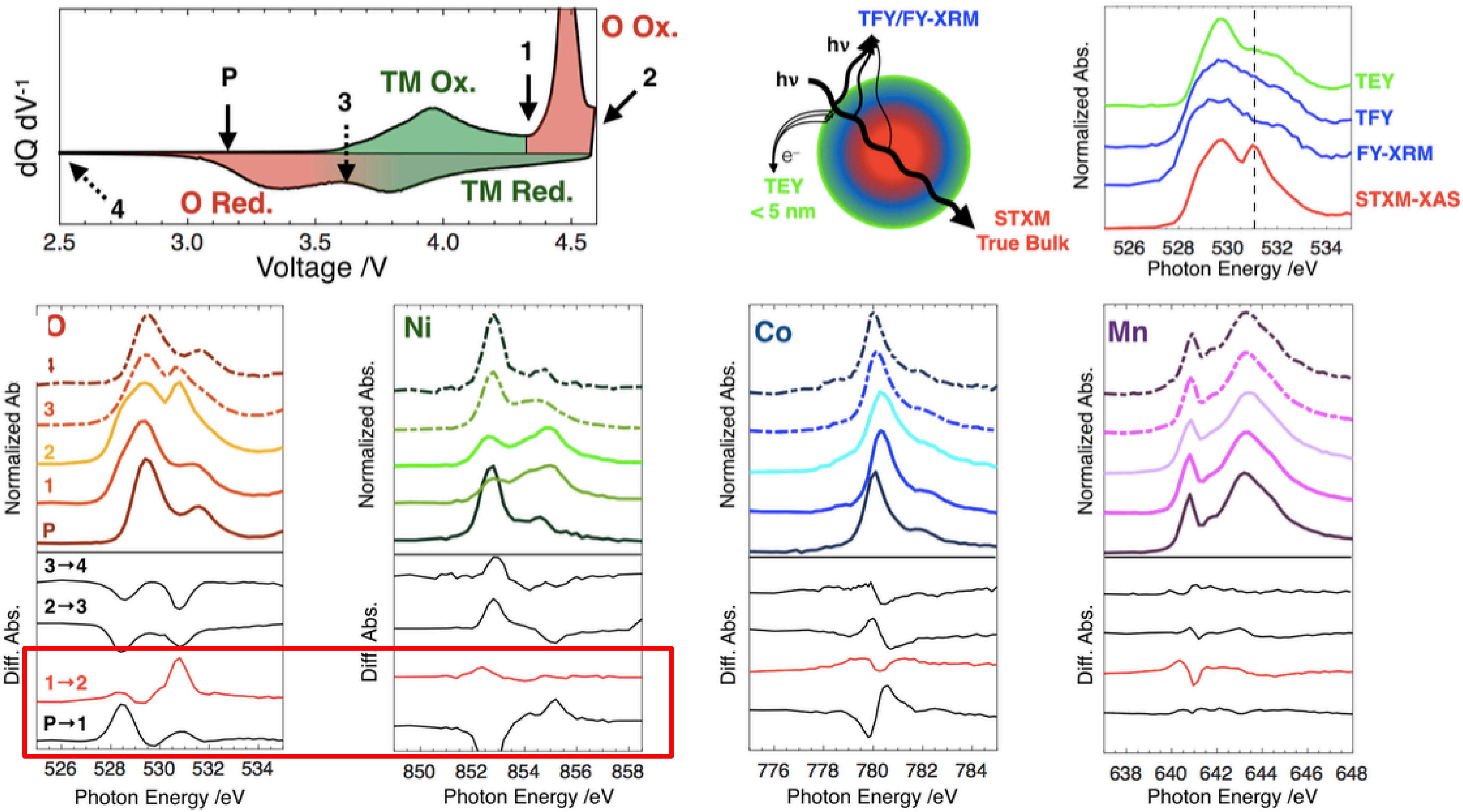
$Li_X(Ni,Mn,Co)O_2$




**Goal**: understand activation and voltage fade mechanisms, particularly with regards to anion redox and oxygen evolution.

# *Activation step:*

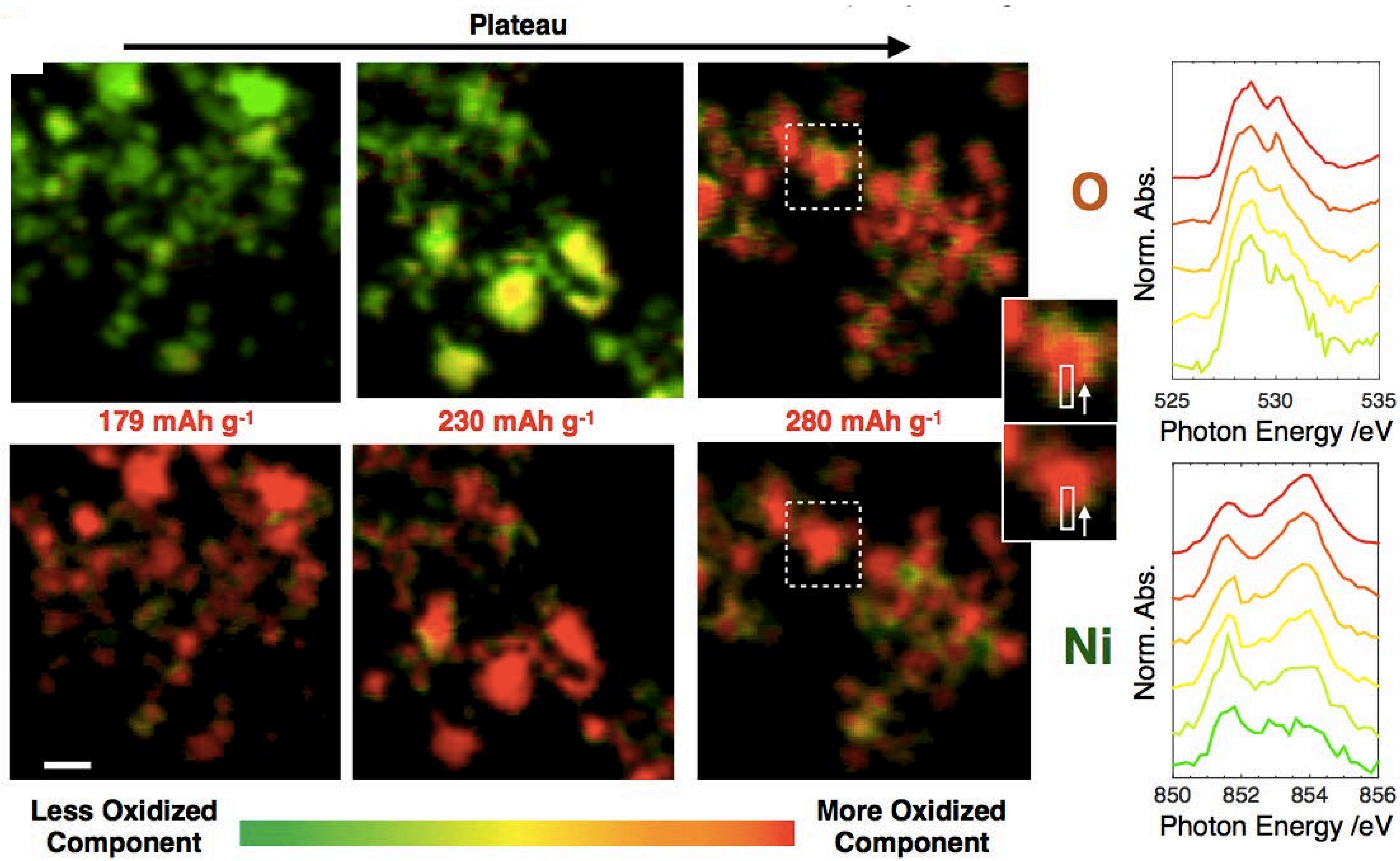
# Two types of 'oxygen' redox




Two types of oxygen redox: **(1)** hybridized TM-O and **(2)** negligibly-hybridized O

# *Activation step:*

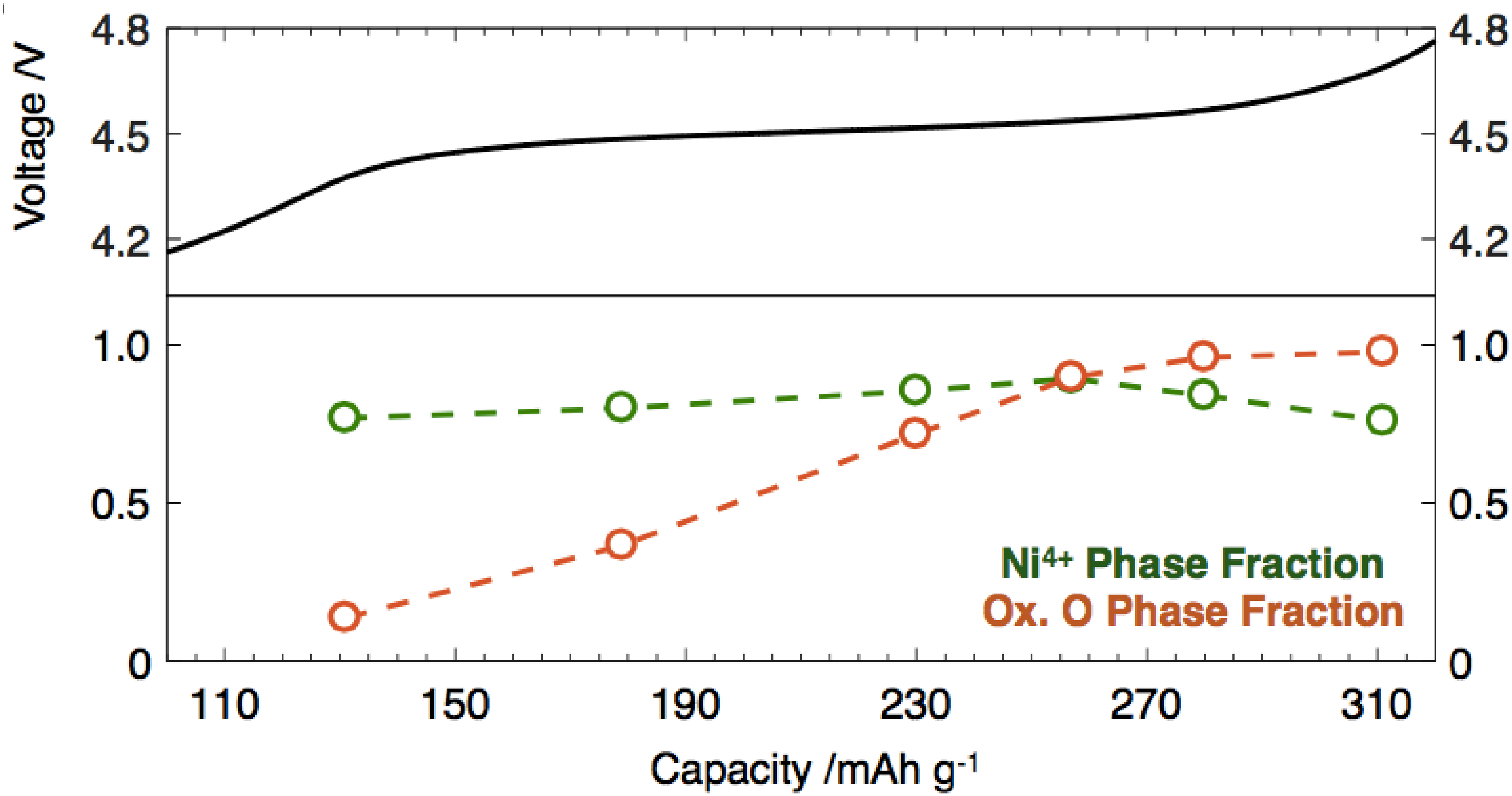
# O redox occurs in the bulk, OER occurs on the surface




O redox occurs uniformly throughout bulk of primary particles; OER occurs at surface leading to Ni reduction.

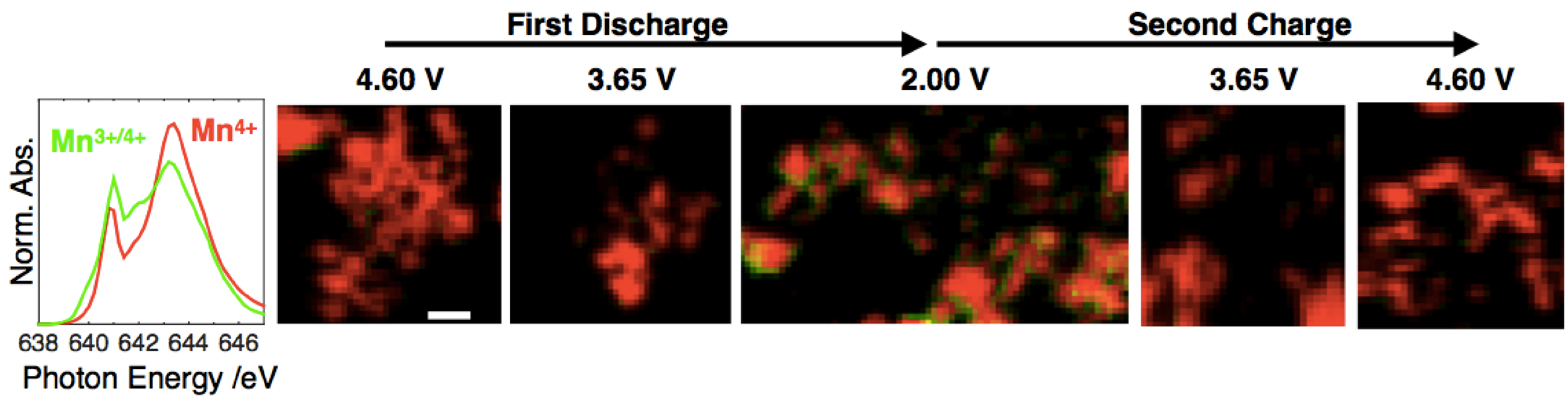
*Activation step:*

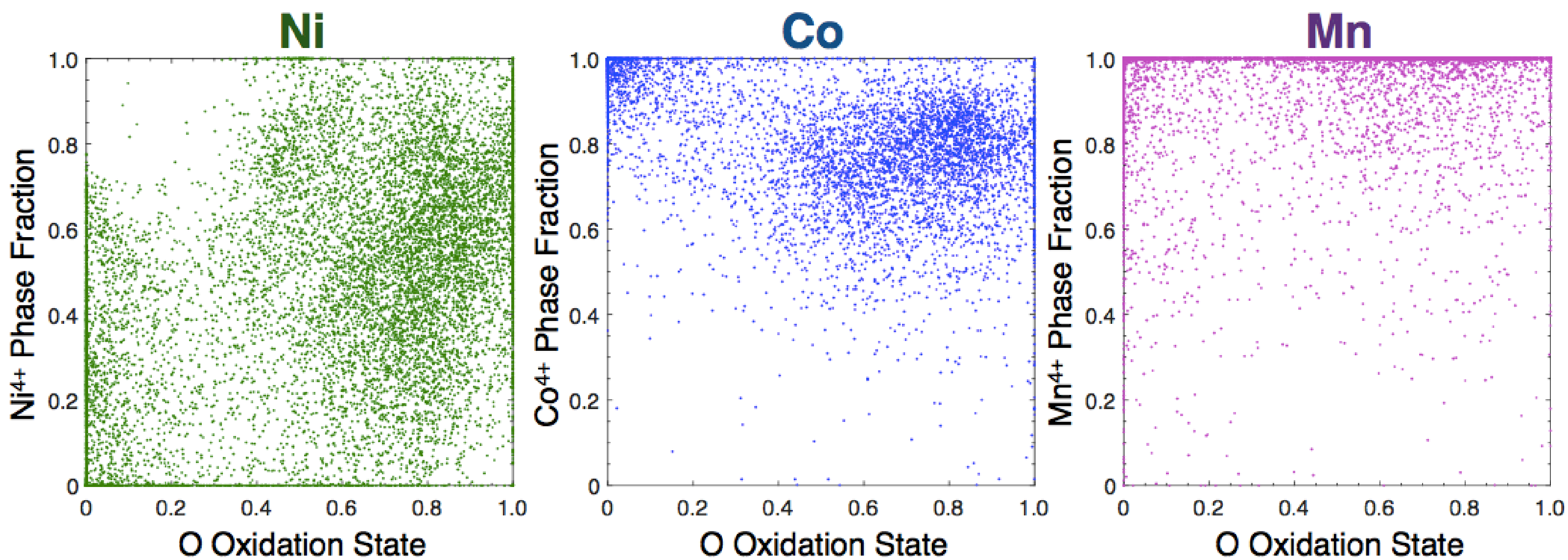
# O redox occurs in the bulk, OER occurs on the surface




O redox occurs uniformly throughout bulk of primary particles; OER occurs at surface leading to Ni reduction.

# *Activation step:*
# O redox occurs in the bulk, OER occurs on the surface

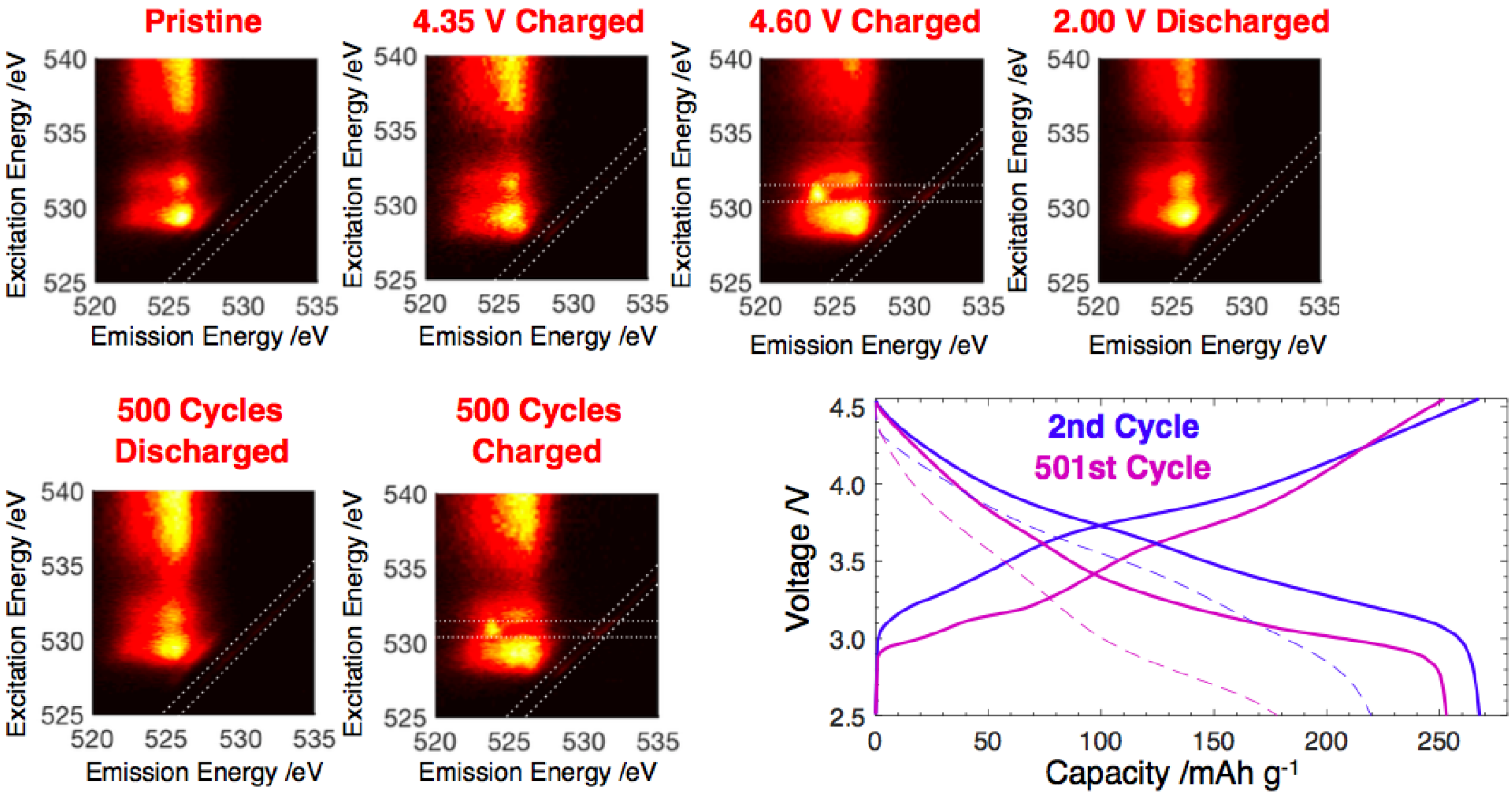



Mn is redox active at the surface during discharge to 2V, consistent with with oxygen-deficient surface phase.

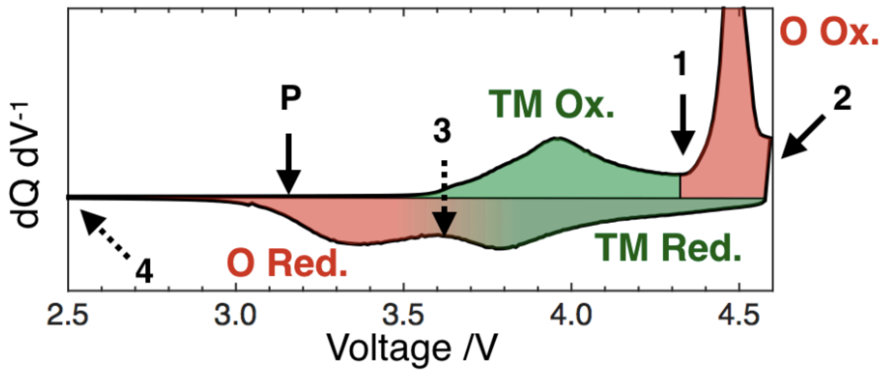
# *Activation step:*

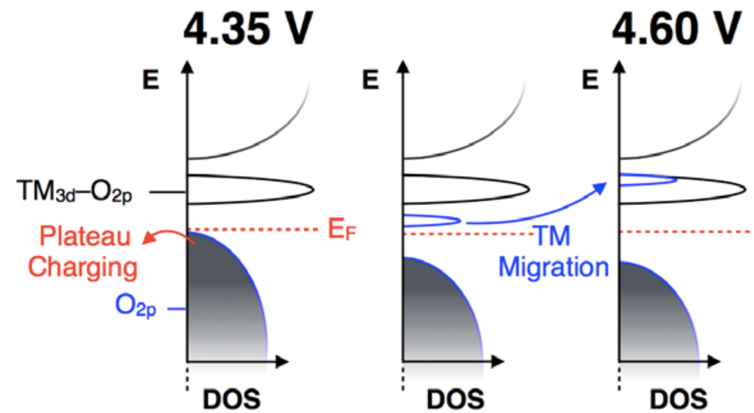
# O redox is stable for 500 cycles

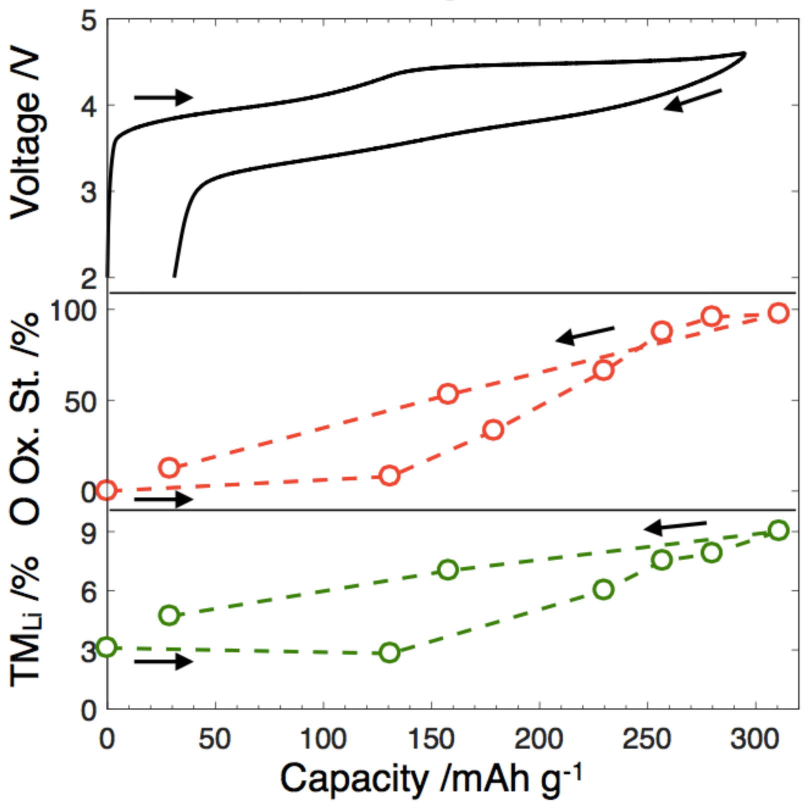



C/68 capacity after 500 1C/2C cycles shows 94% capacity retention & spectroscopy confirms persistent O redox.

# *Activation step:*
# O redox strongly coupled to TM migration




- TM migration during the plateau decreases the O redox potential by > 1V, explaining the hysteresis during first charge.

**Take Home**: Fully visualized the nanoscale redox chemistry, revealing and deconvolving bulk TM-O redox, O redox and OER, and explain the 1st charge/discharge voltage curve. Demonstrate hybridized TM-O redox & negligibly hybridized O redox occur throughout cycling (500 cycles).

# Response to Previous Year Reviewer's Comments

None

# Collaboration & Coordination with Other Institutions

**Advanced Light Source, LBNL**:

- Users facility accessed via proposal (no cost)
- Carry out X-ray microscopy experiments at beam line 11.0.2, 5.3.2
- Carry out resonant inelastic X-ray scattering at beam line 8.0.1

**Molecular Foundry, LBNL**:

- Users facility accessed via proposal (no cost)
- Carry out density functional theory simulations of lithium-excess layered oxides

**Samsung Advanced Institute of Technology**

- Materials for NMC and LMR-NMC

# Remaining Challenges & Barriers

- Translate ex-situ experiment to in-situ for both secondary & primary particles
- Phase transformation in NMC has a very weak spectroscopic signature
- Couple nanoscale mapping to nanoscale crystallography

# Proposed Future Research

- LMR-NMC: quantify anion and cation redox as a function of cycling to fully understand their relationship to capacity and voltage fade
- NMC: connect secondary particle SOC hotspots to stress gradient and preferred particle orientations
- NMC: extend characterization to single particles

# Summary

- NMC: The induced stresses and accompanying SOC heterogeneity have detrimental effect on the material cycle life by accelerating secondary particle fracture and resulting in locally overcharged domains at the cutoff voltage, which was revealed by X-ray microscopy.
- LMR-NMC: X-ray microscopy visualized the nanoscale redox chemistry, revealing and deconvolving bulk TM-O redox, O redox and OER, and explain the 1st charge/discharge voltage curve. Demonstrate hybridized TM-O redox & negligibly hybridized O redox occur throughout cycling (500 cycles).

# Acknowledgement

This work was by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, Battery Materials Research Program, U.S. Department of Energy. We grateful acknowledge the guidance from Tien Duong and David Howell.